



# Amorphization-induced reverse electron transfer in NiB cocatalyst for boosting photocatalytic H<sub>2</sub> production

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## ABSTRACT

Regulating the electron density distribution of active sites to accelerate catalytic process is of great significance to explore high-efficiency cocatalysts for photocatalytic hydrogen production. In this work, a novel strategy of amorphization-induced reverse electron transfer is proposed to optimize the electronic structure of Ni active site in nickel boride (NiB) cocatalyst to promote the photocatalytic hydrogen-production activity of TiO<sub>2</sub>. Herein, the NiB nanodots (0.5–1 nm) with an amorphous structure can perfectly be anchored onto TiO<sub>2</sub> surface via a novel-designed light-induced route. The resulting amorphous-NiB/TiO<sub>2</sub> sample achieves the photocatalytic H<sub>2</sub>-production rate of 2334.0 μmol h<sup>-1</sup> g<sup>-1</sup>, which is 1.8 times higher than that of the traditional crystalline-NiB/TiO<sub>2</sub> photocatalyst. The experimental and theoretical investigations confirm that the amorphization of NiB can induce the reverse electron transfer from B to Ni, which can promote the hydrogen desorption process of the Ni active site to boost the H<sub>2</sub>-production efficiency. This work paves a new way for active site optimization and delivers in-depth insights for the exploration of high-efficient hydrogen-production cocatalysts.

## 1. Introduction

Solar-driven hydrogen (H<sub>2</sub>) production over photocatalysts (TiO<sub>2</sub>, g-C<sub>3</sub>N<sub>4</sub>, ZnIn<sub>2</sub>S<sub>4</sub>, etc.) is an environmentally benign technique to assist the sustainable energy system [1–6]. However, the photocatalytic H<sub>2</sub>-evolution activities of the photocatalysts are inevitably suppressed by the rapid recombination of photoexcited electrons and sluggish interfacial H<sub>2</sub>-generation reaction kinetics [7–10]. As a widely employed strategy, cocatalyst modification can eloquently promote the activities of the above bare photocatalysts by separating the photocarriers and providing reactive sites for the interfacial hydrogen production reaction [11–14]. As for the H<sub>2</sub>-evolution reaction, the hydrogen adsorption/desorption balance on the active sites of cocatalysts should be simultaneously appropriate for fast-capturing atomic hydrogen in the medium and rapidly releasing H<sub>2</sub> to achieve overall high-efficiency H<sub>2</sub> production [15–19]. Unfortunately, the active sites in most studied cocatalysts still exhibit undesirable hydrogen adsorption owing to their inferior electronic configurations, resulting in their limited catalytic activities [20–22]. Therefore, it is essentially important to explore strategies to optimize the electron density distribution of the cocatalyst to optimize

the hydrogen adsorption/desorption balance of the active site for efficient photocatalytic hydrogen production.

At present, transition metal borides (TMBs) have received wide concern in the field of catalysis due to their metalloid electrical conductivity, component adjustability and good thermal stability [23–27]. In particular, nickel boride (NiB) has been widely employed as an effective electrocatalytic water-splitting catalyst because of its low cost and easy accessibility [28–30], and the metallic Ni sites are considered to be the active sites for hydrogen evolution [31,32]. It was reported that the metallic Ni atom on Ni metal cocatalyst usually possesses a strong H adsorption capacity [33,34], which is unfavorable for H<sub>2</sub> desorption in the hydrogen evolution process (Fig. 1a) [35,36]. Unfortunately, after the combination of Ni metal with B to produce crystalline NiB, the Ni active sites inevitably possess an electron-deficient state due to the electron transfer from Ni to B according to Pauling's electronegativity rule, resulting in a stronger H adsorption and slower hydrogen desorption on the Ni site (Fig. 1b) [37,38]. To improve the H<sub>2</sub>-evolution performance of NiB, considerable efforts have been devoted to regulating the electron density distribution of the NiB to optimize the hydrogen desorption on Ni site, such as heterostructure construction and

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heteroatoms introduction [39,40]. For example, it has been recently reported that the construction of Ni<sub>3</sub>B/Ni [41,42] and Ni<sub>3</sub>B/MoB [43] heterojunctions could weaken the hydrogen adsorption of Ni active sites by regulating the electron arrangements at the grain boundaries to promote the H<sub>2</sub>-evolution performance. Another wide-employed strategy is heteroatom doping, such as reported NiCoB [44] and NiFeCoB [45], in which the introduced Fe and Co atoms can optimize the hydrogen desorption of neighbored Ni active sites by donating electrons to Ni. However, the above traditional strategies about the heterostructure construction and heteroatom integration would inevitably suffer from the interference of external substances, which will lead to the decreased stability of the catalytic materials [46]. Therefore, it is urgently vital to develop a sustainable, high-efficient and atom-economic strategy to modulate the electron density distribution of Ni active site in NiB.

Compared with the crystalline structure, it was reported that the amorphization of materials could disturb or even reconstruct the electron density distribution of the active sites by endowing the active sites with appropriate coordination environment [47]. It can be envisioned that the above electronic configuration adjustment by amorphization strategy can dramatically facilitate the catalytic properties of active sites. Unfortunately, this relative strategy is rarely reported in the catalytic field. Motivated by the above concerns, we here present a new strategy of amorphization-induced reverse electron transfer from B to Ni in amorphous NiB, with the purpose of optimizing the hydrogen desorption of Ni active sites in NiB cocatalyst to promote the photocatalytic H<sub>2</sub>-generation activity of TiO<sub>2</sub> (Fig. 1c). In this case, the amorphous NiB (a-NiB) with ultrasmall particle size (0.5 nm) can uniformly be deposited on TiO<sub>2</sub> surface to synthesize a-NiB-modified TiO<sub>2</sub> photocatalyst (a-NiB/TiO<sub>2</sub>) via a novel well-designed photodeposition route. Photocatalytic H<sub>2</sub>-evolution tests found that the a-NiB/TiO<sub>2</sub> (8 %) photocatalyst displayed the optimal activity of 2344.0  $\mu\text{mol h}^{-1} \text{g}^{-1}$ , which is superior to the conventional crystalline NiB-modified TiO<sub>2</sub> (c-NiB/TiO<sub>2</sub>) photocatalyst. XPS investigations and Density Functional Theory (DFT) calculations affirm the reverse electron transfer from B to Ni in the amorphous NiB compared with the conventional crystalline NiB cocatalyst, which can efficiently promote the hydrogen desorption of Ni active sites, thereby boosting the hydrogen-production performance of TiO<sub>2</sub>. To the best of our knowledge, this is the first report on the amorphization-induced reverse electron transfer in the internal NiB for improved photocatalytic hydrogen production. The present amorphization-induced optimization of active sites offers a significant conception to design high-efficient cocatalysts for photocatalytic hydrogen production.

## 2. Experimental sections

### 2.1. Preparation of a-NiB/TiO<sub>2</sub> photocatalyst

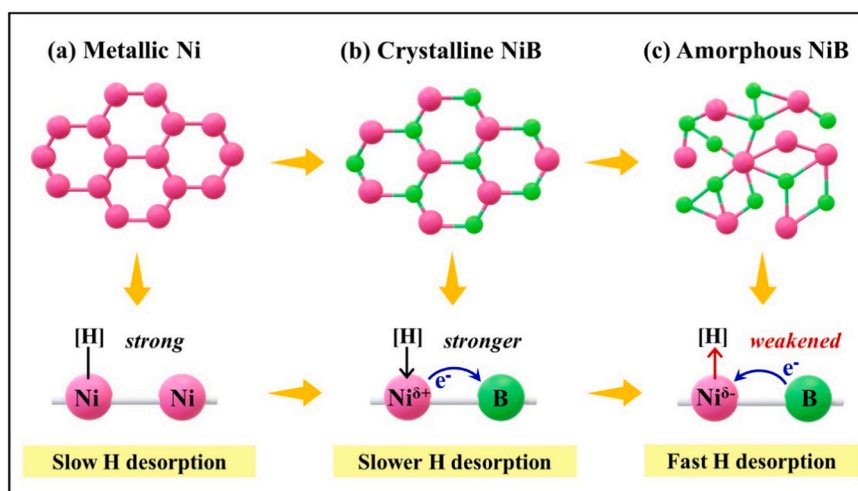
The a-NiB/TiO<sub>2</sub> photocatalysts were prepared by in-situ formation of amorphous NiB on TiO<sub>2</sub> surface via a direct light-induced route. Specifically, 100 mg of TiO<sub>2</sub> powder was first dispersed into 80 mL EtOH solution (25 vol%) to form a suspension, and then a certain amount of Ni (CH<sub>3</sub>COOH)<sub>2</sub> was dissolved into the above suspension under ultrasound. Subsequently, 2 mL of 0.5 M dimethylamine borane (DMAB) solution was injected into the above suspension with magnetic stirring for 10 min. After that, the above system was fully degassed with N<sub>2</sub> for 15 min and irradiated with 4 LED lights (365 nm) to trigger the photodeposition of amorphous NiB on TiO<sub>2</sub> surface. After illuminating for 2 h, the products were filtered, washed and vacuum dried at 55 °C to obtain the a-NiB/TiO<sub>2</sub> photocatalysts. Herein, the weight percentage of Ni element to TiO<sub>2</sub> was set to be 1, 3, 5, 8, 10, and 12 wt%, and the obtained products were named a-NiB/TiO<sub>2</sub>-X, where X represented 1, 3, 5, 8, 10, and 12, respectively. For comparison, the crystalline NiB-modified TiO<sub>2</sub> photocatalyst (c-NiB/TiO<sub>2</sub>) was gained by directly calcining the above a-NiB/TiO<sub>2</sub> sample at argon atmosphere (300 °C, 2 h).

### 2.2. Characterization

The crystal phase properties and morphologies for various samples were analyzed via X-ray diffraction (XRD, Rigaku III), scanning electron microscope (SEM, JSM-7500 F), and transmission electron microscope (TEM, Thermo Fisher). The composition and valence states of elements in the samples are investigated using inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent 730), ex-situ X-ray photoelectron spectroscopy and in-situ irradiated X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). All the XPS binding energies were calibrated by the adventitious carbon C 1 s peak at 284.8 eV. The ultraviolet-visible absorption spectra (UV-vis) were recorded by using a UV-2450 instrument. The time-resolved photoluminescence (TRPL) spectra were collected on a fluorescence lifetime spectrophotometer (FLS920).

### 2.3. Photocatalytic H<sub>2</sub> evolution test

The H<sub>2</sub>-evolution experiments of the photocatalysts were performed in a 100 mL three-neck flat-bottom Pyrex flask at ambient temperature and atmospheric pressure, and the outlets of the flask were sealed with a



**Fig. 1.** The strategy for amorphization of NiB cocatalyst to optimize the H desorption for H<sub>2</sub> production via reversing electron transfer: (a) metallic Ni, (b) crystalline NiB and (c) amorphous NiB.

silicone rubber septum, which is in line with the previous reports [13, 19]. In a typical measurement, 0.05 g of the prepared photocatalyst was dispersed in an aqueous solution with the addition of lactic acid as the sacrificial agent (80 mL, 10 vol%). Then, the flask containing the photocatalyst suspension was subjected to magnetic stirring and ultrasonic treatment, respectively. After purging with nitrogen (15 min), the resulting reactor was illuminated by 4 LED lamps (3 W 365 nm) to realize the photocatalytic  $H_2$  production. After periodical irradiation for 30 min, a gas chromatograph (GC-2014 C) was employed to calculate the amount of generated  $H_2$  to analyze the activities of various photocatalysts.

### 3. Results and discussion

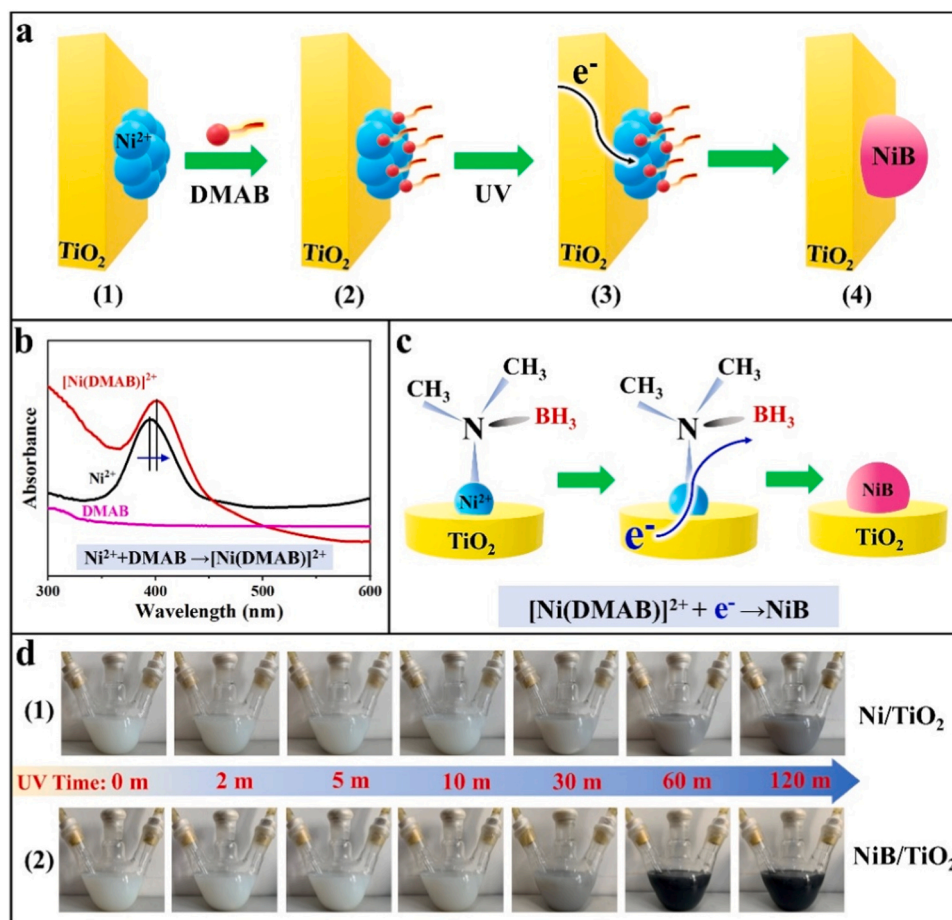
#### 3.1. Synthetic strategy of a-NiB/TiO<sub>2</sub> photocatalyst

The amorphous NiB nanodots are mildly fabricated and synchronously anchored on TiO<sub>2</sub> surface via a photo-triggered electron-reduction route (Fig. 2). Firstly, TiO<sub>2</sub> nanoparticles are dispersed into Ni(Ac)<sub>2</sub> solution to form a uniform suspension, and the positive divalent nickel ions can easily be accumulated on TiO<sub>2</sub> surface via the electrostatic interaction to form Ni<sup>2+</sup>/TiO<sub>2</sub> (Fig. 2a-(1)) [48]. When DMAB is injected to the above system, DMAB can combine the Ni<sup>2+</sup> on TiO<sub>2</sub> surface to form [Ni(DMAB)]<sup>2+</sup> via a chemical complexation attraction, which can be well evidenced by the following UV-visible adsorption results in Fig. 2b [49,50]. In this case, the [Ni(DMAB)]<sup>2+</sup> complex displays an obviously shifted adsorption peak compared to the single Ni<sup>2+</sup> and DMAB solution, strongly verifying the excellent combination of Ni<sup>2+</sup> and

DMAB on TiO<sub>2</sub> surface to form [Ni(DMAB)]<sup>2+</sup>/TiO<sub>2</sub> (Fig. 2a-(2)). Subsequently, after the excitation of UV light (Fig. 2a-(3)), the massive [Ni(DMAB)]<sup>2+</sup> species can finally be in situ reduced to form amorphous NiB nanodots (a-NiB) on TiO<sub>2</sub> surface to gain a-NiB/TiO<sub>2</sub> photocatalyst (Fig. 2a-(4)). Herein, the reductive photoelectron excited by light from TiO<sub>2</sub> can effectively transfer to the surface and induce the mild reduction of [Ni(DMAB)]<sup>2+</sup> complex to form amorphous NiB nanodots on TiO<sub>2</sub> surface (Fig. 2c). The photographs of the color change in different photodeposition stages are shown in Fig. 2d. It can be easily found that compared with the gray color of Ni/TiO<sub>2</sub> suspension (Figs. 2d-(1)), the a-NiB/TiO<sub>2</sub> system (Fig. 2d-(2)) apparently exhibits the dark black after photodeposition, implying the successful realization of black a-NiB cocatalyst on TiO<sub>2</sub> surface to form a-NiB/TiO<sub>2</sub> photocatalyst. By controlling the different concentrations of Ni(Ac)<sub>2</sub> solution, the a-NiB/TiO<sub>2</sub> photocatalyst with various loading amounts of a-NiB cocatalyst can be successfully and precisely prepared through the foregoing photodeposition route.

#### 3.2. Microstructures of a-NiB/TiO<sub>2</sub> photocatalyst

To prove the successful construction of the amorphous NiB nanodot-loaded TiO<sub>2</sub> photocatalyst, the transmission electron microscopy (TEM) characterization is first conducted and the resulting images are shown in Fig. 3. According to the high-resolution TEM images, it can be apparently found that multiple amorphous NiB nanodots with small size of 0.5–1 nm are homogeneously well-attached onto the TiO<sub>2</sub> surface (Fig. 3a). The above fact can further be verified via the following high-angle annular dark field transmission electron microscopic (HAADF-



**Fig. 2.** (a) Graphical illustration for the photosynthesis of a-NiB/TiO<sub>2</sub>. (b) The UV-visible adsorption spectra of various solutions. (c) Graphical illustration for the formation mechanism of amorphous NiB triggered by photoexcited electrons. (d) The photographs of the color change in different photodeposition stages: (1) Ni/TiO<sub>2</sub> and (2) a-NiB/TiO<sub>2</sub>.



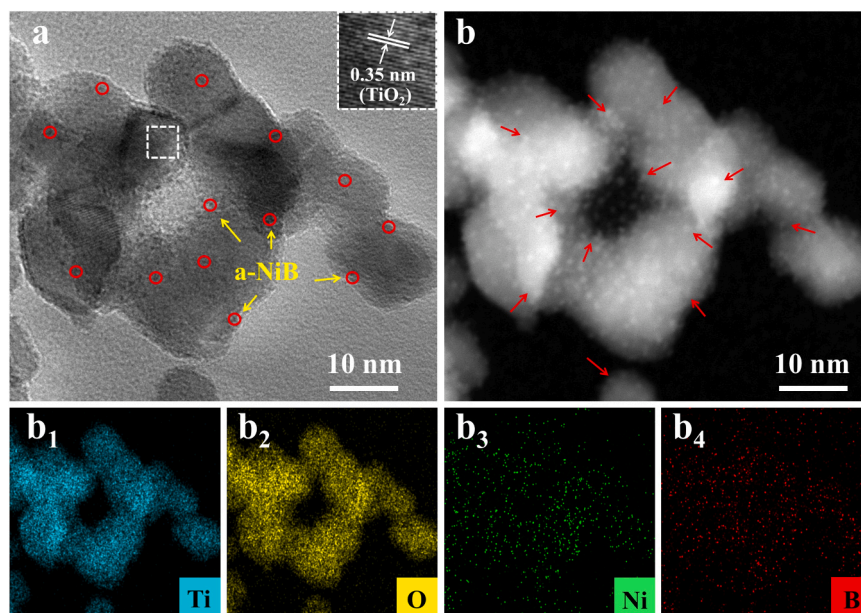


Fig. 3. (a) HRTEM, (b) HAADF-STEM and (b<sub>2</sub>–b<sub>4</sub>) EDS mapping images of the a-NiB/TiO<sub>2</sub> photocatalyst.

TEM) image in Fig. 3b, where plentiful highlighted amorphous NiB nanodots can be easily identified in the corresponding position. Furthermore, the in-situ element mapping results (Fig. 3b<sub>1</sub>–b<sub>4</sub>) reveal that the signals of Ni and B elements are well-distributed with the Ti and O elements and the Ni/B ratio is calculated to be 1.6 according to the ICP-OES result, strongly verifying the successful synthesis of amorphous NiB nanodots on TiO<sub>2</sub> surface.

The XRD, SEM, and UV–vis diffuse reflectance characterizations are further employed to evidence the successful preparation of a-NiB/TiO<sub>2</sub> photocatalyst. As the XRD results displayed in Fig. 4a and Fig. S2, all the cocatalyst-modified TiO<sub>2</sub> photocatalysts show the comparable diffraction signal to the bare TiO<sub>2</sub>, implying the few influence of present synthetic route on the TiO<sub>2</sub> structure [51,52]. In addition, there is no obvious distinction between the SEM images of a-NiB/TiO<sub>2</sub> and bare TiO<sub>2</sub> (Fig. S3), suggesting that the applied photosynthesis has no effect on the morphology [53]. Significantly, according to the slow-scan XRD results in Fig. 4b, it is obvious that compared to the amorphous NiB-/TiO<sub>2</sub> sample, the crystalline NiB/TiO<sub>2</sub> sample obviously shows the characteristic diffraction peak of crystalline Ni<sub>3</sub>B (The peak at 44.1° is related to the rutile TiO<sub>2</sub>), strongly manifesting the successful crystallization of a-NiB/TiO<sub>2</sub> photocatalyst to form c-NiB/TiO<sub>2</sub> sample. To further reveal the above crystallization of amorphous NiB, the pure a-NiB is first prepared, and then calcined to prepare the crystalline c-NiB

(The detailed processes are shown in SI-1). Based on their XRD patterns, it is obvious that compared with the weak and broad amorphous peak of a-NiB, the c-NiB sample shows the strong and sharp Ni<sub>3</sub>B (#48–1223) characteristic peaks, verifying the effective transformation of amorphous NiB to crystalline NiB via the present calcination strategy [54,55]. Furthermore, the UV–vis absorption spectra of various samples are carried out to reveal their optical absorption properties and the results are shown in Fig. 4c. It can be observed that the TiO<sub>2</sub> sample exhibits the absorption boundary of around 390 nm, and the bandgap value can be determined to 3.20 eV (Fig. S5) [56,57]. With the loading of Ni cocatalyst, an obvious enhancement of light absorption (390–700 nm) can be observed, and the color of Ni/TiO<sub>2</sub> sample changes from white to gray (inset in Fig. 3d). When modifying with a-NiB and c-NiB, the resulting a-NiB/TiO<sub>2</sub> and c-NiB/TiO<sub>2</sub> photocatalysts possess further enhanced light absorption and deepened sample color owing to the introduction of black NiB. Moreover, as shown in Fig. S6, with the increase loading amount of a-NiB cocatalyst, the visible light absorption and dark degree of the sample color are gradually increased, indicating that the a-NiB with various loading amount can effectively be modified onto the TiO<sub>2</sub> surface. In summary, the above data strongly verify the successful construction of a-NiB/TiO<sub>2</sub> photocatalyst via the well-designed light-induce deposition procedure.

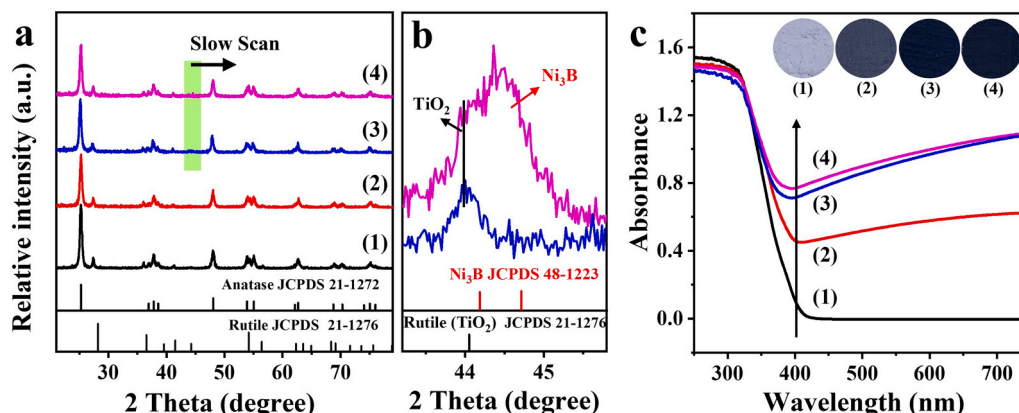
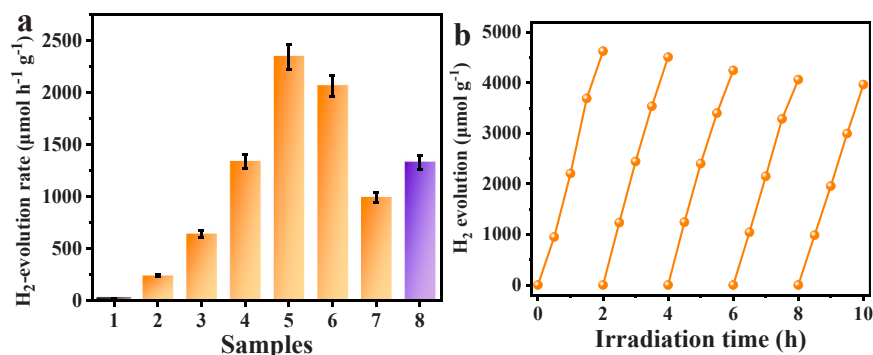


Fig. 4. (a) XRD patterns, (b) slow-scan XRD patterns and (c) UV–vis adsorption spectra of (1) TiO<sub>2</sub>, (2) Ni/TiO<sub>2</sub>, (3) a-NiB/TiO<sub>2</sub> and (4) c-NiB/TiO<sub>2</sub>.



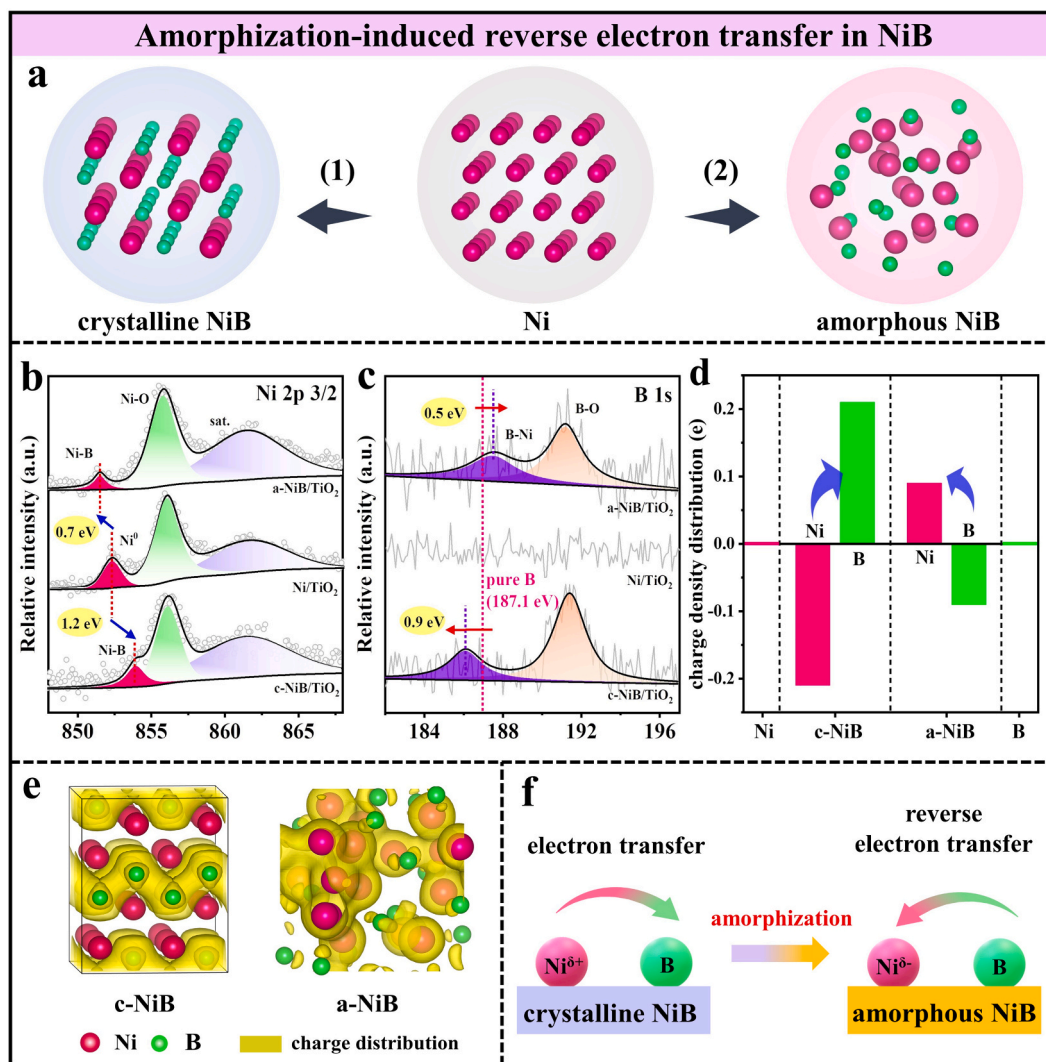


**Fig. 5.** (a) The photocatalytic H<sub>2</sub>-evolution activity of various samples: (1) TiO<sub>2</sub>, (2) a-NiB/TiO<sub>2</sub> (1 wt%), (3) a-NiB/TiO<sub>2</sub> (3 wt%), (4) a-NiB/TiO<sub>2</sub> (5 wt%), (5) a-NiB/TiO<sub>2</sub> (8 wt%), (6) a-NiB/TiO<sub>2</sub> (10 wt%), (7) a-NiB/TiO<sub>2</sub> (12 wt%) and (8) c-NiB/TiO<sub>2</sub>. (b) The cycling runs of the photocatalytic H<sub>2</sub>-evolution activity of the a-NiB/TiO<sub>2</sub> (8 wt%).

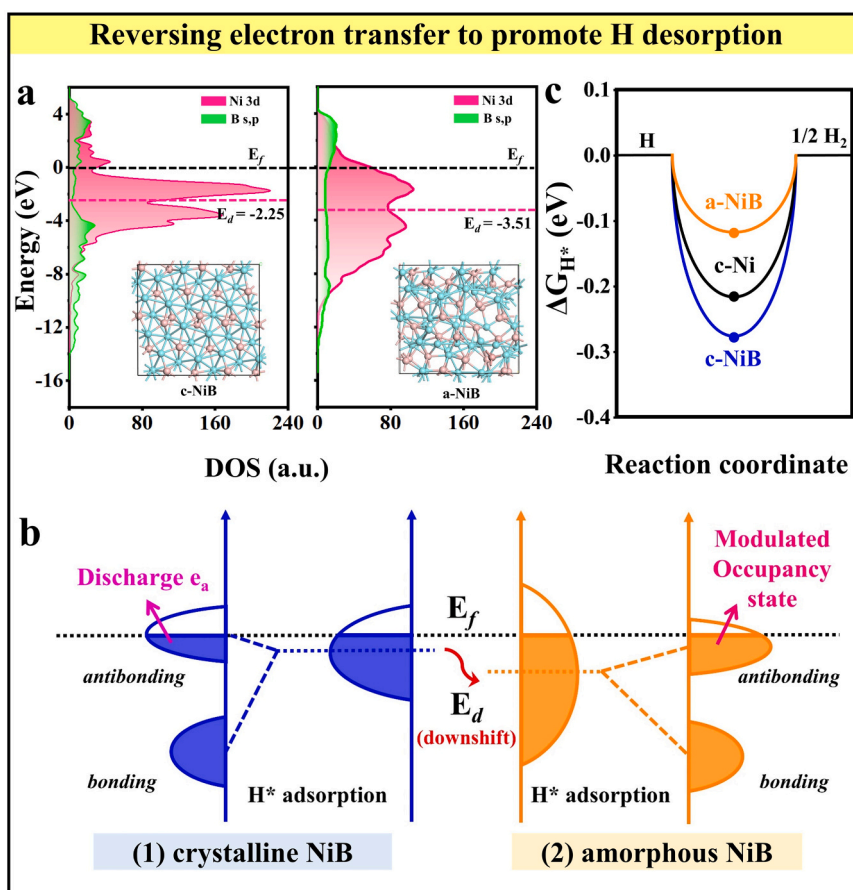
### 3.3. Photocatalytic H<sub>2</sub>-evolution performance and mechanism

The photocatalytic H<sub>2</sub>-evolution activities of the obtained photocatalysts are assessed under UV light of 365 nm with the presence of LA sacrificial agent (10 vol%), as depicted in Fig. 5. The bare TiO<sub>2</sub>

photocatalyst displays the trivial performance of 16.3 μmol h<sup>-1</sup> g<sup>-1</sup>, which can be ascribed to the rapid recombination of carriers and the ineffective catalytic H<sub>2</sub>-generation sites. When a-NiB cocatalyst is modified onto TiO<sub>2</sub>, it can be obviously found that the synthetic a-NiB/TiO<sub>2</sub> photocatalysts possess the tremendous enhancement of H<sub>2</sub>-



**Fig. 6.** (a) Schematic illustration for introducing boron to nickel to form (1) c-NiB and (2) a-NiB. (b-c) The fitted high-resolution XPS spectra of Ni 2p and B 1s for Ni/TiO<sub>2</sub>, c-NiB/TiO<sub>2</sub> and a-NiB/TiO<sub>2</sub>. (d) The Bader charge density distributions of c-NiB and a-NiB. (e) The band decomposed charge density distributions in c-NiB and a-NiB. (f) Schematic illustration for the amorphization-induced reverse electron transfer mechanism in NiB.

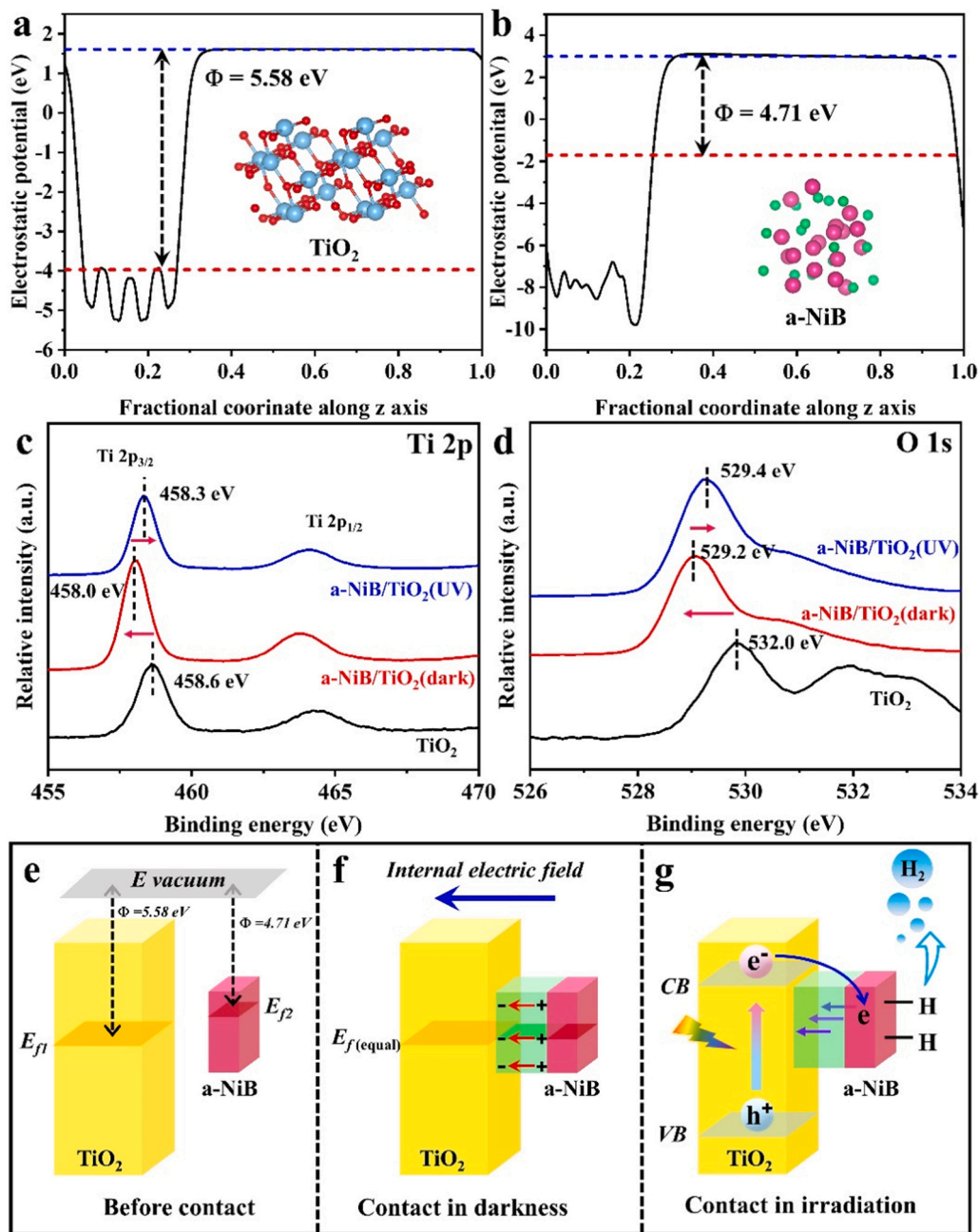


**Fig. 7.** (a) Calculated pDOS and d-band center of c-NiB (left) and a-NiB (right). (b) Schematic illustration for the tailored antibonding-orbital occupancy state of d-band of Ni active site in crystalline and amorphous NiB. (c) The calculated Gibbs free energy barriers for hydrogen adsorption-desorption balance of Ni sites in Ni, c-NiB and a-NiB.

production performance compared to the bare TiO<sub>2</sub>. Particularly, the a-NiB/TiO<sub>2</sub> photocatalyst with the loading amount of 8 wt% shows the optimal photocatalytic H<sub>2</sub>-generation activity of 2344.0  $\mu\text{mol h}^{-1} \text{g}^{-1}$  with an apparent quantum yield (AQY) of 16.3 % (Table S1). Moreover, the cycling performance experiment is employed to study the H<sub>2</sub>-evolution stability of the a-NiB/TiO<sub>2</sub> photocatalyst (Fig. 5b), and the activity of a-NiB/TiO<sub>2</sub> remains stable even after 5 cycling measurements, implying its positive repeatability. Herein, its corresponding turnover number (TON) is calculated to be 42.1 (The detailed calculation is shown in SI-5). It is worth noting that the H<sub>2</sub>-production performance of amorphous NiB/TiO<sub>2</sub> is apparently higher than that of the crystalline NiB/TiO<sub>2</sub> (1330.7  $\mu\text{mol h}^{-1} \text{g}^{-1}$ ), indicating that compared to the crystalline NiB cocatalyst, the amorphization of NiB cocatalyst can effectively boost the photocatalytic H<sub>2</sub>-production activity of TiO<sub>2</sub>. Furthermore, the amorphization strategy of NiB cocatalyst can also efficiently boost the H<sub>2</sub>-evolution activity of g-C<sub>3</sub>N<sub>4</sub>, implying the potential extensibility of amorphous NiB cocatalyst (Fig. S7). Thus, it is necessary to explore the mechanism of the above crystallinity-dependent activity of NiB cocatalyst in the H<sub>2</sub>-evolution process.

According to the above performance test results, it can be found that the amorphization of NiB cocatalyst can efficiently facilitate the H<sub>2</sub>-generation process, which can be attributed to the amorphization-induced reconstruction of electron density distribution in amorphous NiB. To unravel the electron density distribution in crystalline and amorphous NiB, the chemical environment of each element in metallic Ni, crystalline NiB, and amorphous NiB are carefully studied by XPS characterization. According to the XPS results of Ni 2p in Fig. 6b, the Ni/TiO<sub>2</sub> sample exhibits two characteristic peaks of Ni at 852.3 eV and 855.7 eV, corresponding to the zerovalent and bivalent Ni, respectively.

When introducing B into Ni to form crystalline NiB cocatalyst (Fig. 6a-(1)), it can be easily found that the resulting c-NiB/TiO<sub>2</sub> sample show the typical Ni peak at 853.5 eV, which is higher than that of the traditional Ni/TiO<sub>2</sub>. The above positive shift (1.2 eV) of Ni peak in crystalline NiB can be ascribed to the electron transfer from Ni to B, which is caused by the introduction of B with higher electronegativity than Ni. Interestingly, the above results about electron transfer is completely reversed in the amorphous NiB structure (Fig. 6a-(2)). In this case, compared with the conventional Ni/TiO<sub>2</sub> sample, the binding energy of Ni peak on the a-NiB/TiO<sub>2</sub> sample is negatively shifted to 851.6 eV, powerfully proving the fact that the electron of B can reversibly transfer to Ni in the amorphous NiB. In fact, the above-mentioned reverse electron transfer in the amorphous NiB can simultaneously be verified via the XPS results of B 1s, as shown in Fig. 6c. Comparing with the binding energy of pure B (187.1 eV), the elemental B in c-NiB/TiO<sub>2</sub> is negatively shifted by 0.9 eV, while the elemental B in a-NiB/TiO<sub>2</sub> possesses a reversely positive shift of 0.5 eV, which further suggest the phenomenon of amorphization-induced reverse electron transfer in NiB. In addition, the reverse electron transfer mechanism in amorphous NiB can further be theoretically investigated via the following DFT calculation. The crystalline model of c-NiB contains 96 Ni atoms and 72 B atoms, and the atomic ratio of B to Ni is 0.75 (the value is approximate to the ICP-OES result of a-NiB/TiO<sub>2</sub>). Furthermore, the amorphous model of a-NiB is reasonably constructed using a wide-accept “melt-and-quench” approach based on the above c-NiB model via dynamic simulation and geometric optimization, and the optimized models are shown in Fig. S8 (The detailed processes are shown in SI-8). First, as displayed in Fig. 6d, the Bader charge analysis is employed to quantitatively explore the electron transfer between Ni and B atom in crystalline and amorphous



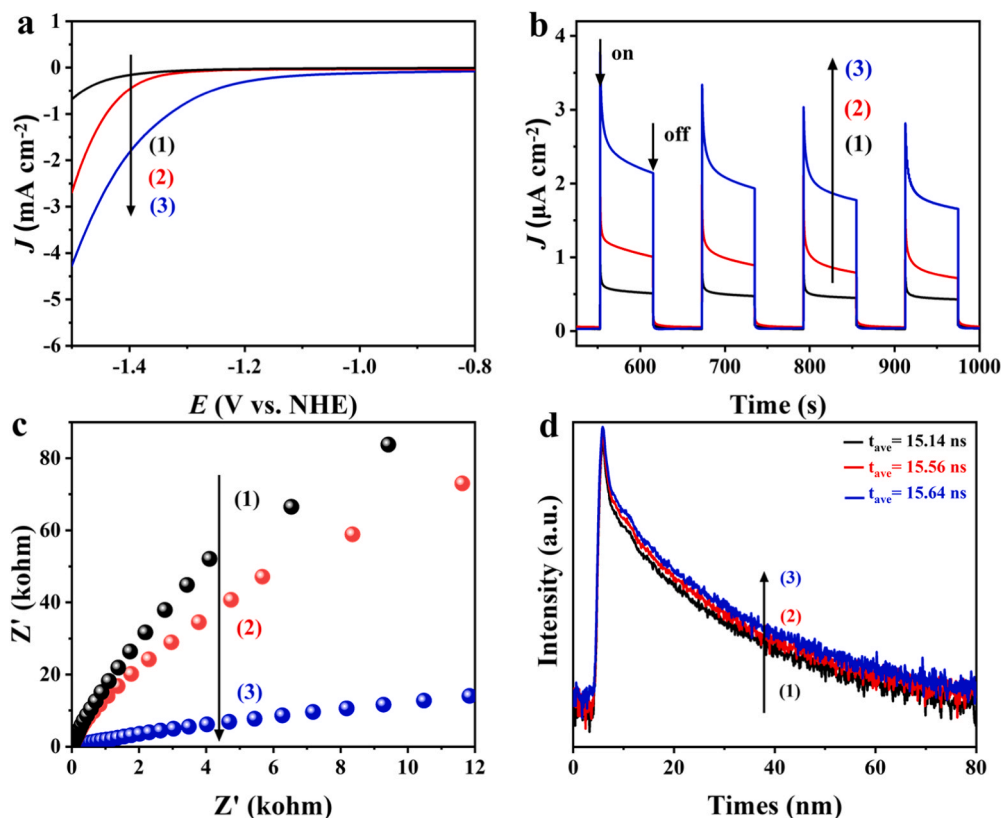
**Fig. 8.** (a-b) Calculated electrostatic potentials for TiO<sub>2</sub> photocatalyst and a-NiB cocatalyst. (c-d) In-situ XPS results of Ti 2p and O 1s for TiO<sub>2</sub>, a-NiB/TiO<sub>2</sub> (dark), and a-NiB/TiO<sub>2</sub> (UV). (e-g) Schematic diagram for the promoted photoelectron transfer from TiO<sub>2</sub> to a-NiB under the enforcement of internal electric field.

NiB. The calculated Bader charge results indicate that Ni atom averagely loses 0.21 electrons ( $|e|$ ) to B in crystalline NiB, but for the amorphous NiB, the Ni atom can conversely gain 0.09 electrons from B, reconfirming the amorphization-induced reverse electron transfer in NiB. Furthermore, the above reverse electron transfer can be visually observed via the band decomposed charge density distributions analysis (Fig. 6e). Clearly, it can be found that compared with the crystalline NiB structure, the simulated charge distribution is mainly accumulated on the Ni site in the amorphous NiB structure, which is in line with the above XPS and Bader charge analysis results. Therefore, based on the above experimental and theoretical results, it can be rationally authenticated the amorphization-induced reverse electron transfer mechanism in NiB, as depicted in Fig. 6f.

The above amorphization-induced reverse electron transfer can effectively adjust the electronic configuration of Ni active site in a-NiB to

promote the interfacial H<sub>2</sub>-desorption process, thereby boosting the H<sub>2</sub>-evolution activity, which can be well investigated via the following projected density of states (pDOS) analysis and  $\Delta G_{H^*}$  calculation. Based on the pDOS results of c-NiB and a-NiB in Fig. 7a, the d-band of Ni atoms is obviously localized near the Fermi level compared with that of s,p-band of B atoms, suggesting that the Ni sites of NiB cocatalyst act as the active site for hydrogen production. Moreover, the above exploration of active sites in NiB can be well achieved via the electrochemical in situ shielding approach (Fig. S9). In this case, after the poison of Ni sites, the current density of NiB greatly decreases, implying that Ni is the feasible active site for photocatalytic H<sub>2</sub> evolution in NiB cocatalyst. Further analysis of the pDOS suggested that compared with the crystalline structure, the amorphous NiB clearly displays a relatively broad and diffused d-band of Ni, which can be ascribed to the strengthened orbital hybridization between Ni 3d and B 2 s-2p states induced by its





**Fig. 9.** (a) linear sweep voltammetry (LSV), (b) transient photocurrent response curves, (c) electrochemical impedance spectra (EIS) and (d) transient-state photoluminescence spectra of (1)  $\text{TiO}_2$ , (2)  $\text{c-NiB/TiO}_2$ , and (3)  $\text{a-NiB/TiO}_2$ .

disordered coordination environment. In this contribution, based on the  $\text{d}$ -band theory as shown in Fig. S10, the broadening of  $\text{d}$ -band in amorphous NiB can significantly induce the downshift of the  $\text{d}$ -band center of Ni, which is in line with the present calculated results of  $\text{d}$ -band center ( $-2.25$  eV for  $\text{c-NiB}$  and  $-3.51$  eV for  $\text{a-NiB}$ ). As a result, with the downshift of the  $\text{d}$ -band center, the antibonding orbitals formed through the interaction of  $\text{Ni-H}_{\text{ads}}$  can be filled by more electrons (Fig. 7b), leading to the promotion of  $\text{H}_2$  desorption on Ni active site, thereby boosting the  $\text{H}_2$ -evolution activity of the amorphous NiB cocatalyst. Furthermore, based on the simulated surface models of  $\text{a-NiB}$  and  $\text{c-NiB}$  in Fig. S11, the free energy change calculation on Ni active site is conducted, as shown in Fig. 7c. As for  $\text{c-NiB}$  cocatalyst, the  $\Delta G_{\text{H}^*}$  of Ni site exhibits an adverse value of  $-0.282$  eV due to the electron transfer from Ni to B, which can induce the decrease of electron density of Ni site, therefore inhibiting the hydrogen desorption process. After amorphization to form NiB cocatalyst, the  $\Delta G_{\text{H}^*}$  of Ni site is obviously optimized to  $-0.138$  eV, indicating the weakening of hydrogen adsorption on Ni, which can boost hydrogen desorption to promote the  $\text{H}_2$ -evolution performance. Therefore, it can be concluded that the amorphization-induced reverse electron of  $\text{a-NiB}$  can modulate the antibonding orbital occupation state of Ni active site to boost the hydrogen desorption process, thereby promoting the interfacial hydrogen evolution reaction.

Aside from boosting interfacial hydrogen evolution reaction, the  $\text{a-NiB}$  cocatalyst can also efficiently boost the separation of photo-generated electrons, which is investigated via the following DFT calculation and in-situ irradiated XPS characterization (Fig. 8). Based on the DFT results in Fig. 8a-b, the calculated work functions ( $\Phi$ ) of  $\text{TiO}_2$  and  $\text{a-NiB}$  are identified to 5.58 and 4.71 eV, respectively (Fig. 8e). When  $\text{TiO}_2$  nanoparticles and  $\text{a-NiB}$  nanodots are contacted in darkness, their  $E_{\text{f}}$  difference can induce the migration of free electrons from  $\text{a-NiB}$  to  $\text{TiO}_2$ , which can be well evidenced by the negative shift of the Ti 2p and O 1s

XPS signals (Fig. 8c-d). As a result of the electron transfer from  $\text{a-NiB}$  to  $\text{TiO}_2$ , an internal electric field directing from  $\text{a-NiB}$  to  $\text{TiO}_2$  is successfully constructed at their interface (Fig. 8f). When the  $\text{a-NiB/TiO}_2$  photocatalyst is irradiated by UV light, the above-constructed internal electric field can effectively boost the separation and transmission of photogenerated electrons to  $\text{a-NiB}$  cocatalyst, which can be revealed by the in-situ irradiated XPS results in Fig. 8b-c and Fig. S12a-b. In this case, compared with the  $\text{a-NiB/TiO}_2$  (dark), the binding energies of Ti (Fig. 8c) and O (Fig. 8d) elements in  $\text{a-NiB/TiO}_2$  (light) shift to a higher value, while the Ni (Fig. S12a) and B (Fig. S12b) elements exhibit a negative shift, strongly demonstrating the flow of the light-excited electrons from  $\text{TiO}_2$  to  $\text{a-NiB}$  cocatalyst during the photocatalytic procedure. Therefore, it can be firmly concluded that the photogenerated electrons of  $\text{TiO}_2$  can be easily transferred to the  $\text{a-NiB}$  cocatalyst to boost the interfacial hydrogen generation (Fig. 8g).

The fast transport of photoexcited electrons and promoted interfacial  $\text{H}_2$ -evolution efficiency of  $\text{a-NiB/TiO}_2$  photocatalyst can further be evidenced via photoelectrochemical measurements and transient-state photoluminescence (PL) spectra (Fig. 9). Based on the LSV curves in Fig. 9a, the current density of the  $\text{a-NiB/TiO}_2$  photocatalyst is obviously larger than that of  $\text{c-NiB/TiO}_2$  and bare  $\text{TiO}_2$ , indicating that the amorphization of NiB cocatalyst can boost the hydrogen-production process. In addition, based on the results of transient photocurrent response (Fig. 9b), electrochemical impedance (Fig. 9c), and TRPL (Fig. 9d), the  $\text{a-NiB/TiO}_2$  sample shows the maximal photocurrent density, minimum impedance, and longest fluorescent lifetime in contrast with other samples, adequately implying the efficient separation and transportation of charges in the  $\text{a-NiB/TiO}_2$  photocatalyst. Thus, the foregoing data demonstrated that the amorphous NiB cocatalyst can efficiently separate and transport photogenerated electrons of  $\text{TiO}_2$  to achieve the promoted interfacial  $\text{H}_2$ -generation process.

## 4. Conclusions

To summarize, amorphous NiB nanodots were successfully fabricated and perfectly anchored onto TiO<sub>2</sub> surface via a well-designed photoinduced route. Photocatalytic H<sub>2</sub>-evolution tests supported that the as-formed a-NiB/TiO<sub>2</sub> shows the superior activity of 2334.0 μmol h<sup>-1</sup> g<sup>-1</sup>, which is 1.8 times over the traditional c-NiB/TiO<sub>2</sub> photocatalyst. The theoretical and experimental results evidenced that the amorphization of NiB cocatalyst can induce the reverse electron transfer from B to Ni, therefore increasing the electron density of Ni active site to optimize its hydrogen desorption process. Consequently, the a-NiB nanodots can work as the effective cocatalyst to fastly transport the photoexcited electron to boost the interfacial H<sub>2</sub>-production reaction, thereby enhancing the photocatalytic H<sub>2</sub>-production activity of TiO<sub>2</sub>. This work not only offers a new method for the synthesis of metal boride-based cocatalysts, but also suggests the amorphization-induced optimization of active sites for hydrogen production.

## CRedit authorship contribution statement

**Haoyu Long:** Methodology, Validation, Writing – original draft. **Duoduo Gao:** Investigation, Visualization. **Ping Wang:** Project administration. **Xuefei Wang:** Data curation, Supervision. **Feng Chen:** Software. **Huogen Yu:** Conceptualization, Resources, Funding acquisition, Writing – review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2023.123270](https://doi.org/10.1016/j.apcatb.2023.123270).

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